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## Surface Magnetism of $\text{Fe}_3\text{O}_4$ Thin Films

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$\text{Fe}_3\text{O}_4$  thin films were prepared by reduction of multilayered  $\alpha\text{-Fe}_2\text{O}_3\text{-SiO}$  films. The thickness dependence of the magnetism of the  $\text{Fe}_3\text{O}_4$  films was investigated by means of the  $^{57}\text{Fe}$  Mössbauer effect and magnetization measurement with a SQUID susceptometer. The saturation magnetization decreased with decreasing film thickness, especially sharply below the thickness of  $\sim 5$  nm. The decrease can be explained consistently by assuming the presence of about 1.5 nm-thick surface layers having a compensated antiferromagnetic spin configuration rather than the well-known ferrimagnetic configuration for bulky  $\text{Fe}_3\text{O}_4$ . This might result from a structural modification in the surface layers of the same type as that proposed for the antiferromagnetic ultrathin films in a previous paper.

KEY WORDS: Multilayered film/ Surface magnetism/  $\text{Fe}_3\text{O}_4$ / Mössbauer effect/

### INTRODUCTION

Recently, fine particles of magnetic materials have been used to achieve high density magnetic recording. Among these spinel ferrites such as  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  are especially important. However, the saturation magnetization of fine particles generally decreases with decrease in particle size.<sup>1,2)</sup> When the particle diameter is below 10 nm, this effect is serious. Morrish et al.<sup>3)</sup> have reported that a non-collinear magnetic structure occurs in the surface layers of  $\gamma\text{-Fe}_2\text{O}_3$  leading to a crucial reduction in magnetization of fine particles. They indicated, moreover, that both the saturation magnetization and the Curie temperature were affected also by the morphology of fine particles.

We have reported the magnetic properties of ultrathin  $\text{Fe}_3\text{O}_4$  films<sup>4)</sup> prepared by a reactive evaporation method to contribute to understanding the magnetism of  $\text{Fe}_3\text{O}_4$  surfaces.

Samples with large surface areas suitable for a study of surface magnetism can be obtained as fine particles or thin films. There are several advantages in using thin films as compared with using fine particles. First, it is comparatively easy to control the surface area to total volume ratio by changing the film thickness, while considerable distribution in the diameter of fine particles is inevitable. Second, though fine particles of  $\text{Fe}_3\text{O}_4$  are very easily oxidized by air even at room temperature, whereas coating to prevent oxidation is easy for films. Coating can be made immediately after the film deposition without breaking the vacuum. Moreover, we can choose an adequate coating material rather freely. It is undesirable that there is an epitaxial relation between the coating material and the  $\text{Fe}_3\text{O}_4$  film,

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because the surface structure and, therefore, the magnetic properties may be modified by coating. We have chosen amorphous and nonmagnetic SiO as a coating substance. According to our experience, even a 1 nm-thick SiO film has superior continuity and flatness.

One  $\text{Fe}_3\text{O}_4$  layer with a thickness of a few nm is not quantitatively enough to be studied by the Mössbauer effect and magnetization measurements. So we have prepared multilayered films of  $\text{Fe}_3\text{O}_4$ -SiO by reduction of  $\alpha\text{-Fe}_2\text{O}_3$ -SiO multilayered films in hydrogen atmosphere. The reducing method has been already reported for the CoO-SiO system.<sup>5)</sup> The reason why we have made use of such an indirect method is to be described in the next chapter.

The most important result we obtained was that films thinner than 5 nm showed antiferromagnetic rather than ferrimagnetic behavior as found by measurements of magnetization and the Mössbauer effect. From the results of electron diffraction and Mössbauer measurements, we have proposed a model cation distribution of  $\text{Fe}_{1.4}^{3+}[\text{Fe}_{0.6}^{3+}\text{Fe}_{1.6}^{2+}]\text{O}_4$  where the number of Fe ions occupying the tetrahedral site is increased remarkably. The antiferromagnetic behavior can be explained by this structural modification. In the present experiment we have prepared  $\text{Fe}_3\text{O}_4$  films with a thickness ranging from 3 nm to 17.5 nm and investigated the magnetic properties by using the Mössbauer effect and a SQUID susceptometer to study the thickness dependence of the magnetic properties. The results have shown that the surface of thick layers also have antiferromagnetic properties as in the previously studied ultrathin  $\text{Fe}_3\text{O}_4$  films.

## EXPERIMENTAL PROCEDURE

### *Sample Preparation*

The  $\text{Fe}_3\text{O}_4$ -SiO multilayered films were prepared by reduction of  $\alpha\text{-Fe}_2\text{O}_3$ -SiO multilayered films. The reason why we have taken the indirect reduction method is the difficulty in thickness control of  $\text{Fe}_3\text{O}_4$  films depositing on an amorphous substrate: a rather high deposition rate of about 1 nm/s was necessary to directly obtain crystalline  $\text{Fe}_3\text{O}_4$  films.

The deposition system is described elsewhere.<sup>6)</sup> The  $\text{Fe}_2\text{O}_3$ -SiO multilayered films were prepared by an alternating reactive evaporation of  $\text{Fe}_2\text{O}_3$  and high vacuum deposition of SiO. The  $\text{Fe}_2\text{O}_3$  films were deposited in an oxygen pressure of  $5 \times 10^{-2}$  Pa and SiO films in a vacuum of  $10^{-4}$  Pa.

As substrates glass and polyimide film were used (glass for X-ray diffraction measurements and polyimide film for Mössbauer effect and SQUID measurements). During deposition, substrates were held at room temperature by water cooling. The deposition rate was monitored by a quartz-oscillating monitor.

By reducing these  $\text{Fe}_2\text{O}_3$ -SiO multilayered films by hydrogen gas,  $\text{Fe}_3\text{O}_4$ -SiO multilayered films were obtained. Temperature of reduction was 250°C and the hydrogen flow rate was 150 ml/min. The thickness of the SiO layers was set at 1.5 nm.

The samples used for measurements are listed in Table I.

Table I. List of Prepared Samples

Sample No.	Thickness of $\text{Fe}_3\text{O}_4$	Layering Time	Measurement
SF1	3.0 nm	10	X-ray Diffraction
SF2	3.0 nm	1	Electron Diffraction
SF3	5.0 nm	1	Electron Diffraction
SF4	10.0 nm	1	Electron Diffraction
SF5	3.0 nm	20	Mössbauer Spectroscopy, SQUID
SF6	5.6 nm	20	Mössbauer Spectroscopy, SQUID
SF7	8.5 nm	18	Mössbauer Spectroscopy, SQUID
SF8	12.0 nm	13	Mössbauer Spectroscopy, SQUID
SF9	17.5 nm	10	Mössbauer Spectroscopy, SQUID

*Sample Characterization*

The multilayered structure of the films was investigated by X-ray diffraction using  $\text{Cu-K}\alpha$  (RIGAKU RU-200). The artificial periodic structure could be observed by small-angle X-ray diffraction, that is the Bragg peak corresponding to the total periodic thickness of  $\text{Fe}_3\text{O}_4$  and  $\text{SiO}$  layers.

Magnetic properties of  $\text{Fe}_3\text{O}_4$ - $\text{SiO}$  multilayered films were investigated by  $^{57}\text{Fe}$  Mössbauer effect and SQUID susceptometer (SHE corporation) measurements.

The crystal structure within one layer of  $\text{Fe}_3\text{O}_4$  was investigated by transmission electron microscopy (JEOL JEM-100CX). Samples for the TEM study was prepared as follows. A film of  $\text{SiO}$  about 20 nm thick was deposited on a cleaved (100) surface of  $\text{NaCl}$ . The  $\text{SiO}$  film was removed from  $\text{NaCl}$  with water and mounted on a mesh to be set in the electron microscope. One layer of  $\text{Fe}_2\text{O}_3$  was deposited on it and then 2 nm-thick  $\text{SiO}$  was deposited on the  $\text{Fe}_2\text{O}_3$  film subsequently. This composite film was reduced with hydrogen at  $250^\circ\text{C}$ .

**RESULTS AND DISCUSSION***X-ray Diffraction*

The as-deposited  $\alpha\text{-Fe}_2\text{O}_3$ - $\text{SiO}$  multilayered film was colored vermilion and transparent. Figure 1 (a) shows the low angle X-ray diffraction pattern for sample  $[\text{Fe}_2\text{O}_3 (3 \text{ nm})\text{-SiO} (1.5 \text{ nm})] \times 10$ . The 1st order Bragg peak corresponding to the total thickness of  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}$  was observed, which indicated that the layer thickness of both  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}$  was precisely controlled and the flatness of the layer was fairly good. The reduced  $\text{Fe}_3\text{O}_4$ - $\text{SiO}$  multilayered film was black. Figure 1 (b) shows the low angle X-ray diffraction pattern for the reduced  $[\text{Fe}_3\text{O}_4 (3 \text{ nm})\text{-SiO} (1.5 \text{ nm})] \times 10$  (SF1). The hydrogen reduction did not destroy the periodic structure and the periodicity had nearly the same value as expected from the small change of about 3% in volume before and after reduction. During the reduction the  $\text{SiO}$  layers were stable.

*Electron Diffraction of Thin  $\text{Fe}_3\text{O}_4$  Films*

In Fig. 2 electron diffraction patterns for samples SF2~SF4 are shown. The

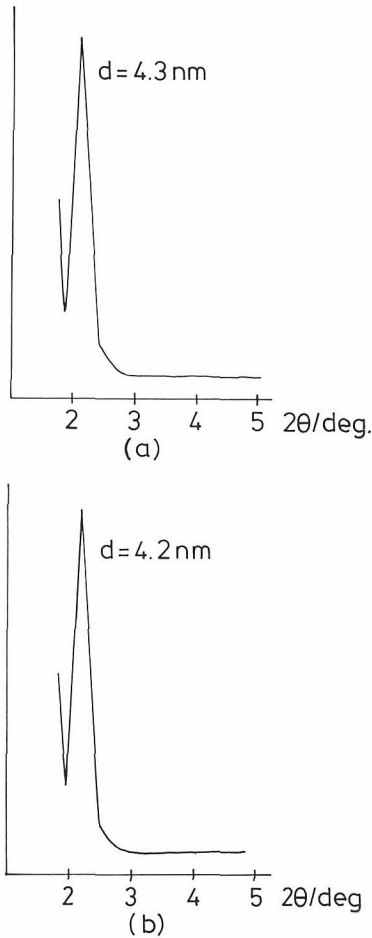


Fig. 1. (a) Low angle X-ray diffraction pattern of the as-deposited  $[\alpha\text{-Fe}_2\text{O}_3(3\text{ nm})\text{-SiO}(1.5\text{ nm})] \times 10$ . (b) Low angle X-ray diffraction pattern of the reduced  $[\text{Fe}_3\text{O}_4(3\text{ nm})\text{-SiO}(1.5\text{ nm})] \times 10$ .

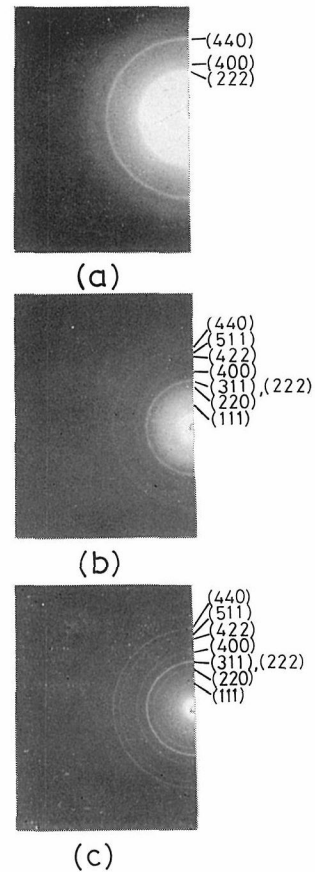


Fig. 2. Electron diffraction patterns of (a) SF2, (b) SF3 and (c) SF4.

ring patterns indicated that the  $\text{Fe}_3\text{O}_4$  films consisted of randomly oriented fine crystallites. The sharp pattern for the 10 nm thick sample (SF4) corresponded to the well-known spinel structure, while the rings tended to become broadened with decrease of the film thickness. At last, for the 3 nm thick  $\text{Fe}_3\text{O}_4$  (SF2) diffraction rings corresponding to (111), (220), (311), (422), (511) became very weak but the (222), (400) and (440) rings remained, indicating that the unit cell for this sample had a half lattice constant as compared with that of the usual spinel structure. This was explained in our previous paper by assuming a change in the Fe ion distribution to be described below.

The spinel structure consists of oxygen layers close packed along the  $\langle 111 \rangle$  direction, the Fe ions partially filling the tetrahedral A and octahedral B sites. There are two filling modes, I and II, alternating with each other along

$\langle 111 \rangle$ . In I, both the A and B sites are quarter filled, while in II three quarters of the B sites only are filled. The formation of the half-sized unit cell in our samples has been thought to result from a tendency that the distribution of the Fe ions becomes random with decreasing film thickness so that the difference between the successive Fe layers become less significant. The most important modification in Fe ion distribution has been supposed to be such a partial occupancy by  $\text{Fe}^{3+}$  ions of the A sites in the layer "II" as leading to the total structure of  $\text{Fe}_{1.4}^{3+}[\text{Fe}_{0.6}^{3+}\text{Fe}_{1.0}^{2+}]\text{O}_4$  as reported in our previous paper.

#### *Magnetism of Thin $\text{Fe}_3\text{O}_4$ Films*

The magnetic properties of  $\text{Fe}_3\text{O}_4$  films are to be shown and interpreted in this chapter. Here, we refer to the essential points in advance for simplicity. Various experimental results indicated consistently the presence of antiferromagnetic surface layers extending to the depth of about 1.5 nm. Figure 3 illustrates sche-

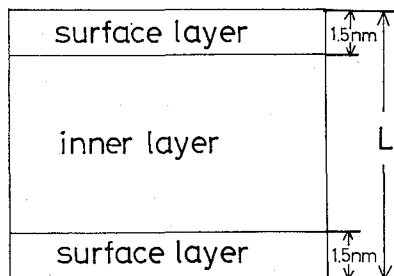


Fig. 3. Schematic illustration of the film structure model of the  $\text{Fe}_3\text{O}_4$  film. The film consists of antiferromagnetic surface layers extending to the depth of about 1.5 nm and bulky inner layer.

matically the idealized film structure. It should be noted that the crystallite dimension within a layer estimated by TEM observation is much larger than the thickness. The surface layers have such an unusual Fe-ion distribution as in extremely thin films and show antiferromagnetic behavior, while the inner layers have the normal  $\text{Fe}_3\text{O}_4$ -type structure and the corresponding large magnetization. The most relevant experimental result is the thickness dependence of the magnetization and the Mössbauer spectra measured at 4.2 K.

In Fig. 4 Mössbauer spectra taken at room temperature for samples SF5~SF9 are shown. Above the Verwey transition temperature (120 K),  $\text{Fe}_3\text{O}_4$  shows a magnetic hyperfine spectrum with two sets of six lines. One is from  $\text{Fe}^{3+}$  in the A sites and the other is from  $\text{Fe}^{2.5+}$  in the B sites. Sample SF9 shows an almost bulky spectrum, except that the values of the internal fields of 483 kOe for  $\text{Fe}^{3+}(\text{A})$  and 457 kOe for  $\text{Fe}^{2.5+}(\text{B})$  are slightly small as compared with the bulk values of 495 kOe for  $\text{Fe}^{3+}(\text{A})$  and 470 kOe for  $\text{Fe}^{2.5+}(\text{B})$ . However, a superparamagnetic relaxation effect becomes dominant with the decrease of the film thickness and finally at the thickness of about 3 nm, the spectrum shows no hyperfine field.

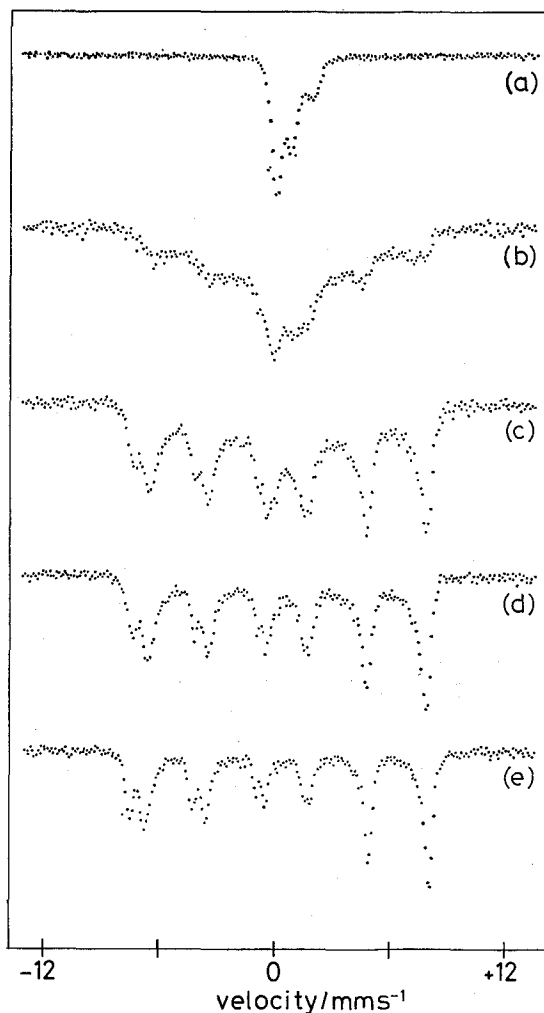


Fig. 4. Mössbauer absorption spectra taken at room temperature for samples (a): SF5, (b): SF6, (c): SF7, (d): SF8, (e): SF9.

In Fig. 5 the dependence of the magnetization on the film thickness observed at room temperature in a field of 30 kOe is shown. The variation of the saturation magnetization shows an abrupt drop below 5 nm. A rather similar dependence was observed even at 4.2 K as shown below where the superparamagnetic effect was expected to be absent.

Figure 6 shows that the magnetization observed at 4.2 K in a field of 30 kOe decreases with decreasing thickness, especially sharply below 5 nm. The magnetization of bulky  $\text{Fe}_3\text{O}_4$  to be compared with amounts to 98 emu/g at 4.2 K. A more microscopic observation by the Mössbauer effect at the same temperature (Fig. 7) indicates, first of all, that it is not appropriate to attribute the small magnetization to the presence of paramagnetic Fe ions as can be seen from the rather well-defined magnetic hyperfine splitting for the 3 nm-thick sample. The magnetic hyperfine

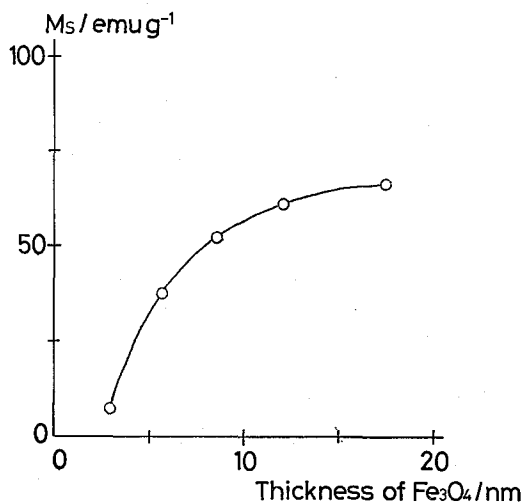


Fig. 5. Thickness dependence of the magnetization in a field of 30 kOe at room temperature for the same samples in Fig. 4.

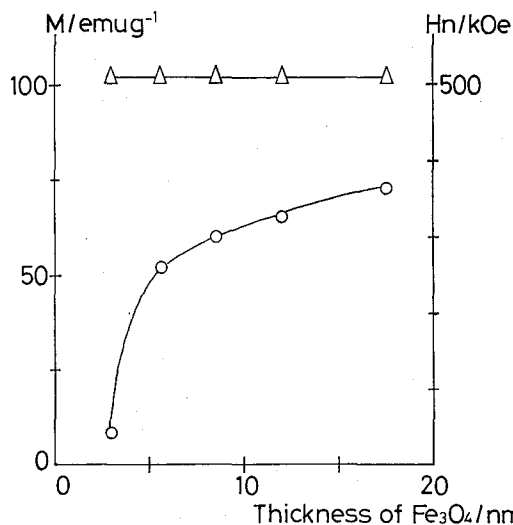


Fig. 6. Thickness dependence of the magnetization in a field of 30 kOe (○) and the internal field of  $\text{Fe}^{3+}$  in A site (Δ) at 4.2 K for the same sample in Fig. 4.

field is large enough, as compared in Fig. 6 with that for thicker films, to allow us to assume that the sublattice magnetization is fully saturated. It is characteristic that a broad background absorption on which magnetically split peaks are superimposed becomes less important with increasing thickness: a fine structure due to different valences,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  becomes clearer, and the spectrum of sample SF9, 17.5 nm thick, is very similar to that of bulky  $\text{Fe}_3\text{O}_4$  reported by Hargrove et al.<sup>7)</sup> It seems that  $\text{Fe}^{2+}$  ions mainly contribute to the background absorption. This is reasonable because  $\text{Fe}^{2+}$  ions having nonvanishing orbital angular momentum



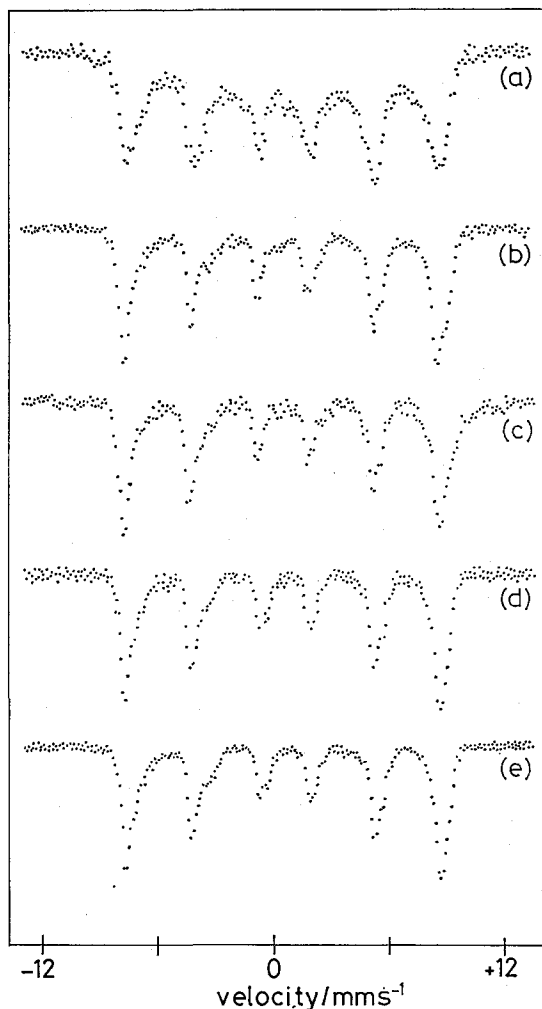


Fig. 7. Mössbauer absorption spectra taken at 4.2 K for the same samples in Fig. 4.

are generally much more sensitive to disordering in the surroundings. These magnetic and Mössbauer effect results indicate definitely that the Fe ions in the thinnest film are antiferromagnetically ordered.

Figure 8 shows the effect of a large external field of 45 kOe on the Mössbauer spectra at 4.2 K. The  $\gamma$ -ray beam runs parallel to the external field in our experiment. To begin with sample SF9, the application of the external field adds 45 kOe to the magnetic hyperfine field of the  $\text{Fe}^{3+}$  ions at the A sites and subtracts 45 kOe from that of the  $\text{Fe}^{3+}$  ions at the B sites to give a clear splitting of the first and the sixth magnetic peaks located at around  $-8$  mm/s and  $+8$  mm/s. The peak intensities of the second and the fifth peaks at around  $-4$  mm/s and  $5$  mm/s are decreased by the selection rule for the transitions, because the sublattice magnetization and, therefore, the magnetic hyperfine fields tend to be aligned along the external field:

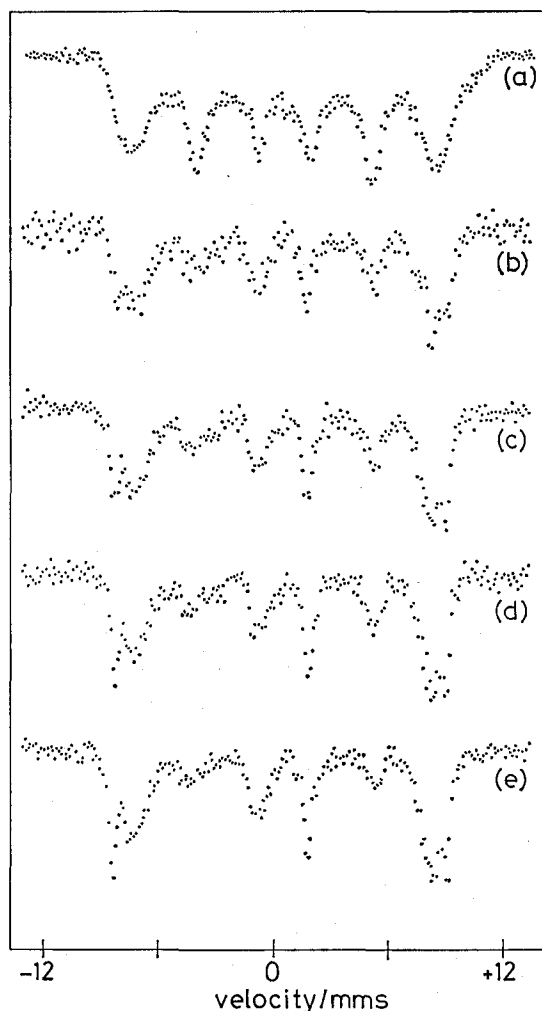


Fig. 8. Mössbauer absorption spectra taken at 4.2 K with an external field of 45 kOe for the same samples in Fig. 4.

it is known that in bulky  $\text{Fe}_3\text{O}_4$  the fifth line completely disappears. With decreasing thickness these effects become obscurer as can be seen most typically for the thinnest sample. The strong fifth peak for the thinnest sample can be attributed to the antiferromagnetic character: in a polycrystalline antiferromagnetic substance the sublattice magnetization can be aligned along an external field only when it is strong enough to overcome the most important antiferromagnetic interaction.

Both the thickness dependence of the magnetization (Fig. 6) and the Mössbauer spectra in the presence of an external field (Fig. 8) can be explained consistently by assuming the model structure shown in Fig. 3: the surface has antiferromagnetic character, while the inner layers are ferrimagnetic. In Fig. 9 the ratio of the measured magnetization to the literature value for bulky  $\text{Fe}_3\text{O}_4$  (98 emu/g) are marked by circles. These are to be compared with the calculated values of

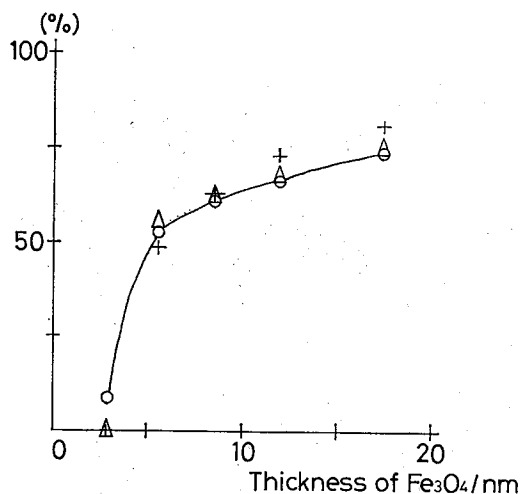


Fig. 9. Thickness dependence of the following ratios: O,  $M/M_{\text{bulk}}$  at 4.2 K;  $\Delta$ ,  $r$  (the ratio of core layers to total film derived from the Mössbauer spectra); +,  $(L-3)/L$  (the ratio of the core layers to total film if the surface layer would be 1.5 nm).

$(L-3)/L$ , where  $L$  stands for the total thickness in units of nm for each sample and  $(L-3)$  corresponds to the thickness of the inner layers. Marked by triangles are  $r=1-3A_5/2A_6$ , where  $A_5/A_6$  refers to the experimental peak intensity ratio of the fifth and sixth absorption lines estimated from the spectra in Fig. 8. Then,  $r$  corresponds to the thickness ratio of the inner layers, which do not contribute to the fifth peak, to the total layers including the surface layers for which  $r=0$  ( $A_5/A_6=2/3$ ). The agreement between the two experimental and one calculated data are very satisfactory.

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